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REACTIONS OF FREE RADICALS AND UNSYMMETRICAL ORGANO-MERCURIC COMPOUNDS

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THE benzoyl peroxide-initiated reaction of carbon tetrachloride and symmetrical organo-mercuric compounds has been reported to be as follows:[1]

$$R_2Hg + CCl_4 \longrightarrow RHgCl + RCCl_3$$

In the present study the homolytical exchange reaction was used between fully substituted unsymmetrical organo-mercuric compounds (prepared by the method of K.A.Kocheshkov and R.Kh.Freidlina) and compounds Nos. 1, 2 and 3, following the Grignard method.

Constants for the compounds are presented in the Table. RHgR' compounds react with carbon tetrachloride in the presence of peroxide according to the scheme:

$$(C_6H_5COO)_2 \longrightarrow C_6H_5COO^{\bullet} + C_6H_5^{\bullet} + CO_2$$

$$C_6H_5^{\bullet} + CCl_4 \longrightarrow C_6H_5Cl + CCl_3^{\bullet}$$

$$RHgR' + CCl_3^{\bullet} \longrightarrow R'Hg^{\bullet} + RCCl_3$$

$$R'Hg^{\bullet} + CCl_4 \longrightarrow R'HgCl + CCl_3^{\bullet} \text{ and so on}$$

$$2CCl_3^{\bullet} \longrightarrow CCl_3 - CCl_3 \text{ the chain break}$$

[1] A.E.Borisov, Izv.Akad.Nauk SSSR,Otdel.khim.nauk 524 (1951).

The less electronegative radical always remains attached to mercury in $RHgCl$[2] and the more electronegative one converts to $RCCl_3$. In the case of R and R' radical characteristics close spacing, as in No.7, all four possible combinations $RHgCl$, $R'HgCl$, $RCCl_3$ and $R'CCl_3$, result.

Thus the $\dot{C}Cl_3$ free radical attacks the same mercury attached radical, which undergoes electrophylic attack by hydrogen ions during acid decomposition of RHgR'.

No.	Original compounds	Melting points	Isolated compounds and yields (%)
1	$C_6H_5HgC_2H_5$	Oil	C_2H_5HgCl(87%) + $C_6H_5CCl_3$
2	$C_6H_5CH_2HgC_4H_9$	Oil	$C_6H_5CH_2HgCl$(73%) + $C_4H_9CCl_3$(58%)
3	$C_6H_5HgC_4H_9$	Oil	C_4H_9HgCl(76%) + $C_6H_5CCl_3$(72%)
4	$C_6H_5HgC_6H_{11}$	59 - 61°	$C_6H_{11}HgCl$(83%) + $C_6H_5CCl_3$(43%)
5	$C_6H_5HgCH_2C_6H_5$	Oil	$C_6H_5CH_2HgCl$(73%) + $C_6H_5CCl_3$(33%)
6	$C_6H_5HgC_6H_4CH_3$-p	167 - 192°	C_6H_5HgCl(88%) + p-$CH_3C_6H_4CCL_3$(82%)
7	p-$CH_3C_6H_4HgC_6H_4CH_3$-o	159 - 189°	o-$CH_3C_6H_4HgCl$(57%) + o-$CH_3C_6H_4CCl_3$(40%) + p-$CH_3C_6H_4HgCl$(43%) + p-$CH_3C_6H_4CCl_3$(60%)
8	$C_6H_5HgC_{10}H_7$-α	165 - 195°	C_6H_5HgCl(73%) + α-$C_{10}H_7CCl_3$(73%)

[2] M.S.Kharasch and R.Marker, J.Amer.Chem.Soc. 48, 3130 (1926); A.N.Nesmeyanov and K.A.Kocheshkov, Uch.Zap.Mosk.Univ. No.3, 283 (1934).